PESTICIDE SURFACE WATER AND SEDIMENT QUALITY REPORT

MAY 2005 SAMPLING EVENT



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Pesticide Monitoring Project Report May 2005 Sampling Event

Summary

As part of the District's quarterly ambient monitoring program, unfiltered water and sediment samples from 36 sites were collected from May 23 to May 27, 2005, and analyzed for over sixty pesticides and/or products of their degradation. The herbicides 2,4-D, ametryn, atrazine, bromacil, diuron, hexazinone, metolachlor, norflurazon, and simazine, along with the pesticide degradates atrazine desethyl, atrazine desisopropyl, and endosulfan sulfate were detected in one or more of these surface water samples. However, none of the concentrations exceeded numeric or calculated criteria

The herbicides ametryn, atrazine, and bromacil, together with the insecticides/degradates aldrin, chlordane, DDD, DDE, DDT, dieldrin, alpha endosulfan, beta endosulfan, endosulfan sulfate, and two PCB compounds were found in the sediment at several locations. The chlordane, two DDD and four DDE compound sediment concentrations were of a magnitude considered to have a harmful effect to freshwater sediment-dwelling organisms.

The compounds and concentrations found are typical of those expected from an area of intensive historical and contemporary agricultural activity.

Background and Methods

The District's pesticide monitoring network includes stations designated in the Settlement Agreement, the Lake Okeechobee Protection Act Permit, and the non-Everglades Construction Project (non-ECP) permit. The District's canals and marshes depicted in Figure 1 are protected as Class III (fishable and swimmable) waters, while Lake Okeechobee and a segment of the Caloosahatchee River are protected as a Class I drinking water supply. Water Conservation Area 1 (WCA1) and the Everglades National Park are also designated as Outstanding Florida Waters, to which anti-degradation standards apply. Surface water and sediment are sampled quarterly and semiannually, respectively, upstream at each structure identified in the permit or agreement.

Sixty-seven pesticides and degradation products were analyzed for in samples from all of the 36 sites (Figure 1). The analytes, their respective method detection limits (MDLs), and practical quantitation limits (PQLs) are listed in Table 1. All the analytical work is performed by the Florida Department of Environmental Protection (FDEP) Central Laboratory in Tallahassee, Florida. Analytical method details can be found at the following location: http://www.dep.state.fl.us/labs/cgi-bin/sop/chemsop.asp. The reader is referred to the *Quality Assurance Evaluation* section of this report for a summary of any limitations on data validity that might influence the utility of these data.

Each pesticide's description and possible uses and sites of application described herein, are taken from Hartley and Kidd (1987). The Florida Ground Water Guidance Concentrations (FGWGC) (FDEP, 1994) are listed to provide an indication at what level these pesticide residues could possibly impact human health, based on drinking water consumption or other routes of exposure (e.g., inhalation, ingestion of food residues, or dermal uptake). Primary ground water standards

are enforceable standards, not screening tools or guidance levels. To evaluate the potential impacts on aquatic life, due to the pulsed nature of exposure, the maximum observed concentration is compared to the Criterion Maximum Concentration published by the United States Environmental Protection Agency (USEPA) under Section 304 (a) of the Clean Water Act, if available, or the lowest effective concentration (EC₅₀) or lethal concentration (LC₅₀) reported in the summarized literature. Sediment concentrations are compared to freshwater sediment quality assessment guidelines (MacDonald Environmental Sciences, LTD., and United States Geological Survey, 2003). A value below the threshold effects concentration (TEC) should not have a harmful effect on sediment-dwelling organisms. Values above the probable effect concentration (PEC) demonstrate that harmful effects to sediment-dwelling organisms are likely to be frequently or always observed. This summary covers surface water and sediment samples collected from May 23 to May 27, 2005.

Results

At least one pesticide was detected in surface water at 34 of the 36 sites and in sediment at 14 of the 34 sites. Sediment samples are not collected at GORDYRD and CR33.5T. Site S332 was deleted from the network since it isn't operational due to the new configuration and operation of upstream canals and pumps. The concentrations of the pesticides detected at each of the sites are summarized for the surface water and sediment in Tables 2 and 3, respectively. All of these compounds have previously been detected in this monitoring program.

The sediment chlordane, DDE, and DDD concentrations at S2 and S6, as well as the chlordane and DDE concentrations at S5A and S3, were of a magnitude considered to represent detrimental effects to sediment-dwelling organisms in freshwater sediments.

The above findings must be considered with the caveat that pesticide concentrations in surface water and sediment may vary significantly in relation to the timing and magnitude of pesticide application, rainfall events, pumping and other factors, and that this was only one sampling event. The possible long-term or chronic toxicity impacts are also reported based on the single sampling event and do not take into account previous monitoring data.

Usage and Water Quality Impacts

2,4-D: 2,4-D is a selective systemic herbicide used for the post-emergence control of annual and perennial broad leaf weeds in terrestrial (grassland, established turf, sugarcane, rice, and on non-crop areas) as well as aquatic areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that 2,4-D (1) has minimum loss from soil by surface adsorption, with a moderate loss by leaching and surface solution; (2) is slightly toxic to mammals and relatively non-toxic to fish; and (3) does not bioaccumulate significantly. The only 2,4-D concentration was detected in the surface water at S191 (3.3 micrograms per liter $[\mu g/L]$) (Table 2). Using these criteria, this observed level should not have an acute impact on fish or aquatic invertebrates. No sediment detections of 2,4-D were found.

<u>Aldrin</u>: Aldrin is a non-systemic insecticide with contact, stomach, and respiratory action, used primarily to control soil insects. Its use and manufacture has been discontinued in the United States. Environmental fate and toxicity data in Tables 4 and 5 indicate that aldrin (1) is relatively

toxic to mammals and fish; and (2) due to the large hydrophobicity of this compound, results in a significant bioconcentration factor. Freshwater sediment quality assessment guidelines have not been developed for aldrin due to insufficient data. The only aldrin concentration detected in sediment was 2.9 micrograms per kilogram ($\mu g/Kg$) at S2. No surface water detections of aldrin were found.

Ametryn: Ametryn is a selective terrestrial herbicide registered for use on sugarcane, bananas, pineapple, citrus, corn, and non-crop areas. Most algal effects occur at concentrations > $10 \mu g/L$ (Verschueren, 1983). Environmental fate and toxicity data in Tables 4 and 5 indicate that ametryn (1) is lost from soil relatively easily by leaching, surface adsorption, and in surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 14.1 milligrams per liter (mg/L) for goldfish (Hartley and Kidd, 1987). The ametryn surface water concentrations found in this sampling event ranged from 0.010 to 0.022 $\mu g/L$. Using these criteria, these observed surface water levels should not have an acute, detrimental impact on fish or aquatic invertebrates. The highest sediment concentration detected was $18 \mu g/Kg$ at S5A. However, no freshwater sediment quality assessment guidelines have been developed for ametryn.

Atrazine: Atrazine is a selective systemic herbicide registered for use on pineapple, sugarcane, corn, rangelands, ornamental turf and lawn grasses, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that atrazine (1) is easily lost from soil by leaching and in surface solution, with moderate loss from surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC₅₀ of 76 mg/L for carp, 16 mg/L for perch and 4.3 mg/L for guppies (Hartley and Kidd, 1987). Also, in a flow-through bioassay, the maximum acceptable toxicant concentration (MATC) of atrazine was 90 and 210 µg/L for bluegill and fathead minnow (Verschueren, 1983). The draft ambient aquatic life water quality criteria identify a one-hour average concentration that does not exceed 1,500 µg/L more than once every three years on the average (USEPA, 2003). The atrazine surface water concentrations found in this sampling event at 32 of the 36 sampling locations, ranged from 0.012 to 3.3 µg/L. Using these criteria, these observed surface water levels should not have an acute or chronic detrimental impact on fish or invertebrates. Only a TEC level (0.30 µg/Kg) has been developed for atrazine concentrations in freshwater sediments. The detected sediment concentration of atrazine at S5A (16 µg/Kg) exceeds this value and it is uncertain if this level will have the possibility for impacting sediment-dwelling freshwater organisms.

Atrazine desethyl (DEA) and atrazine desisopropyl (DIA) are biotic degradation products of atrazine. These degradation products are both persistent and mobile in water; however, DEA is more stable and the dominant initial metabolite. Since DEA and DIA are structurally and toxicologically similar to atrazine, the concentrations of total atrazine residue (atrazine + DEA + DIA) may also be a significant consideration in the surface water environment. The DEA to atrazine ratio (DAR), on a molar basis, has been suggested as an indicator of nonpoint-source pollution of groundwater (Adams and Thurman, 1991) and as a tracer of ground water discharge into rivers (Thurman et al., 1992). Goolsby et al. (1997) determined that low DAR values, median <0.1, occur in streams during runoff shortly after application of atrazine. Higher DAR

values, median about 0.4, occur later in the year after considerable degradation of atrazine to DEA has occurred in the soil. The low median DAR ratio (0.1) at the locations where both atrazine and DEA were detected, suggests minimum degradation of atrazine (Table 6). The highest DAR value 0.4 suggests that considerable degradation of atrazine has occurred in the S140 basin. However, these general guidelines were developed based on observations in Midwest watersheds in northern temperate climates with different soil and water management regimes as well as higher atrazine water concentrations. Applications to the South Florida environment should be made with caution.

Bromacil: Bromacil is a terrestrial herbicide registered for use on pineapple, citrus, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that bromacil (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC₅₀ of 164 mg/L for carp (Hartley and Kidd, 1987). The highest concentration of bromacil detected in the surface water during this sampling event was at C25S99 (0.72 μ g/L). Using these criteria, these observed levels should not have an acute or chronic detrimental impact on fish. Bromacil was detected only in the sediment at G123 (82 μ g/Kg). However, no freshwater sediment quality assessment guidelines have been developed for bromacil.

Chlordane: Chlordane is a chlorinated hydrocarbon previously used as a contact insecticide. Environmental fate and toxicity data in Tables 4 and 5 indicate that chlordane (1) is moderately toxic to mammals and highly toxic to fish; and (2) has the potential for significant bioconcentration. Freshwater sediment quality assessment guidelines identified a TEC of 3.2 $\mu g/Kg$ and PEC of 18 $\mu g/Kg$ for chlordane. All the detected sediment residues are at a concentration (greater than 50 $\mu g/Kg$) where harmful effects to sediment-dwelling organisms are frequently or always observed. While the use of this compound has been discontinued in recent years, its persistence and tendency to accumulate in sediments makes chlordane a compound of concern. Chlordane was not detected in the surface water.

<u>DDD</u>, <u>DDE</u>, <u>DDT</u>: DDE is an abbreviation of **d**ichloro**d**iphenyldichloro**e**thylene [2, 2-bis (4-chlorophenyl)-1, 1-dichloroethene]. DDE is an environmental dehydrochlorination product of DDT (**d**ichloro**d**iphenyl**t**richloroethane), a popular insecticide for which the USEPA cancelled all uses in 1973. The large volume of DDT used, the persistence of DDT, DDE and another metabolite, DDD (**d**ichloro**d**iphenyl**d**ichloroethane), and the high K_{oc} of these compounds account for the frequent detections in sediments. The large hydrophobicity of these compounds also results in a significant bioconcentration factor (Table 4). In sufficient quantities, these residues have reproductive effects in wildlife and carcinogenic effects in many mammals.

The DDD sediment concentrations detected range from 12 to 33 $\mu g/Kg$. Any concentration which would fall below the TEC (4.9 $\mu g/Kg$) should not impact sediment dwelling organisms while concentrations above the PEC (28 $\mu g/Kg$), frequently or always have the possibility for impacting sediment-dwelling organisms. The sediment concentrations detected at S6 (28 $\mu g/Kg$) and S2 (33 $\mu g/Kg$) exceeded the PEC. DDD was not detected in the surface water.

The TEC is $3.2 \mu g/Kg$ and the PEC is $31 \mu g/Kg$ for DDE in freshwater sediments. The concentrations of DDE detected at S2, S3, S5A, and S6 exceed the PEC and frequently or always have the possibility for impacting sediment-dwelling organisms. DDE was not detected in the surface water.

The DDT concentration detected (13 μ g/Kg at S2) exceeds the TEC (4.2 μ g/Kg) but is less than the PEC (63 μ g/Kg). It is uncertain if this level will have the possibility for impacting sediment-dwelling freshwater organisms. No DDT was detected in the surface water.

<u>Dieldrin</u>: Dieldrin is a non-systemic insecticide with all uses canceled in the United States. The high K_{oc} and low water solubility accounts for dieldrin's affinity for sediment. The hydrophobicity of this compound also results in a significant bioconcentration factor and the potential for a high degree of accumulation in aquatic organisms (Table 4). Dieldrin is highly toxic to mammals. The dieldrin concentrations detected (2.4 and 3.3 μ g/Kg) exceed the TEC (1.9 μ g/Kg) but are less than the PEC (62 μ g/Kg). It is uncertain if this level will have the possibility for impacting sediment-dwelling freshwater organisms. No dieldrin was detected in the surface water.

<u>Diuron</u>: Diuron is a selective, systemic terrestrial herbicide registered for use on sugarcane, bananas, and citrus. Environmental fate and toxicity data in Tables 4 and 5 indicate that diuron (1) is easily lost from soil in surface solution, with moderate loss from leaching or surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC₅₀ of 25 mg/L for guppies (Hartley and Kidd, 1987). Crustaceans are affected at lower concentrations with a 48-hour LC₅₀ of 1.4 mg/L for water fleas and a 96-hour LC₅₀ of 0.7 mg/L for water shrimp (Verschueren, 1983). Most algal effects occur at concentrations > 10 μg/L (Verschueren, 1983). The only surface water concentration of diuron found during this sampling event was 0.78 μg/L at G94D (Table 2). Using these criteria, this level should not have an acute, harmful impact on fish or algae. Diuron was not detected in the sediment.

Endosulfan: Endosulfan is a non-systemic insecticide and acaricide registered for use on many crops, including beans, tomatoes, corn, cabbage, citrus, and ornamental plants. Technical endosulfan is a mixture of the two stereoisomeric forms, the α (alpha) and the β (beta) forms. Endosulfan is highly toxic to mammals, with an acute oral LD₅₀ for rats of 70 mg/Kg (Table 4). The Soil Conservation Service (SCS) rates endosulfan with an extra small potential for loss due to leaching, a large potential for loss due to surface adsorption and a moderate potential for loss in surface solution (Table 4). β endosulfan's water solubility and Henry's constant indicate volatilization may be significant in shallow waters. The bioconcentration factors indicate a low to moderate degree of accumulation in aquatic organisms (Table 4). Endosulfan (α and β) was detected only in the sediment at two locations (S177 and S178) in the South Miami-Dade farming area (Table 2). However, no sediment quality assessment guidelines have been developed. Endosulfan was not detected in the surface water.

<u>Endosulfan sulfate</u>: Endosulfan sulfate is an oxidation metabolite of the insecticide endosulfan. The water solubility and Henry's constant indicate that endosulfan sulfate is less volatile than

water and concentrations will increase as water evaporates (Table 4). Endosulfan sulfate has a relatively high degree of accumulation in aquatic organisms (Table 4). The endosulfan sulfate detections occurred at S178 (0.035 μ g/L and 63 μ g/Kg) and S177 (4.9 μ g/Kg). However, no FDEP surface water standard (FAC 62-302) or sediment quality assessment guideline has been promulgated for endosulfan sulfate.

Hexazinone: Hexazinone is a non-selective contact herbicide that inhibits photosynthesis. Registered uses include sugarcane, pineapple, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that hexazinone (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Hexazinone is practically non-toxic to freshwater invertebrates with an EC₅₀ of 145 mg/L for *Daphnia magna* (USEPA, 1988). The highest surface water concentration detected in this sampling event at G94D (1.7 μ g/L) should not have an acute impact on fish or aquatic invertebrates. No hexazinone was detected in the sediment.

Metolachlor: Metolachlor is a selective herbicide used on potatoes, sugarcane, and some vegetables. Environmental fate and toxicity data in Tables 4 and 5 indicate that metolachlor (1) has a large potential for loss due to leaching and a medium potential for loss in surface solution and due to surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Metolachlor is non-toxic to birds (Lyman et al., 1990). The highest surface water concentration found in this sampling event $(0.11 \,\mu\text{g/L} \,\text{at S7})$ is several orders of magnitude below the calculated chronic action level. Using these criteria, the observed level should not have a harmful impact on fish or aquatic invertebrates. No metolachlor was detected in the sediment.

Norflurazon: Norflurazon is a selective herbicide registered for use on many crops including citrus. Environmental fate and toxicity data in Tables 4 and 5 indicate that norflurazon (1) is easily lost from soil surface solution and a moderate potential for loss due to leaching and surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data includes a LC_{50} of >200 mg/L for catfish and goldfish (Hartley and Kidd, 1987). The norflurazon surface water concentrations ranged from 0.024 to 1.1 μ g/L. Even at the highest concentration, this is several orders of magnitude below the calculated chronic action level. Using these criteria, these observed levels should not have an acute, detrimental impact on fish or aquatic invertebrates. Norflurazon was not detected in the sediment.

<u>PCBs</u>: Polychlorinated biphenyls (PCBs) is the generic term for a group of 209 congeners that contain a varying number of substituted chlorine atoms on one or both of the biphenyl rings. PCB-1242 and PCB-1254 are commercial grade mixtures containing 42 percent and 54 percent chlorine by weight. Production of PCBs was banned in 1978 and closed system uses are being phased out. In natural water systems, PCBs are found primarily sorbed to suspended sediments due to the very low solubility in water (Callahan et al., 1979). The tendency of PCBs for adsorption increases with the degree of chlorination and with the organic content of the adsorbent. While the production ban, phase out of uses, and stringent spill clean-up

requirements have significantly reduced environmental loadings in recent years, the persistence and tendency to accumulate in sediment and bioaccumulate in fish, make this class of organochlorine compounds especially problematic. The TEC and PEC are $60~\mu g/Kg$ and $680~\mu g/Kg$, respectively, for total PCBs. Three sediment residues detected fall between the TEC and PEC (S79, S6, and S80), which therefore have a possibility for impacting freshwater sediment-dwelling organisms. None of the PCB congeners were detected in the surface water.

Simazine: Simazine is a selective systemic herbicide registered for use on many crops including sugarcane, citrus, corn, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that simazine (1) is easily lost from soil by leaching and has a moderate potential for loss due to surface adsorption and surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC₅₀ of 49 mg/L for guppies (Hartley and Kidd, 1987). Most of the aquatic biological effects occur at concentrations > 500 μ g/L (Verschueren, 1983). Aquatic invertebrate LC₅₀ toxicity ranges from 3.2 mg/L to 100 mg/L for simazine (USEPA, 1984). The highest surface water concentration of simazine detected at GORDYRD (0.12 μ g/L) was below any level of concern for fish or aquatic invertebrates. No simazine was detected in the sediment.

Quality Assurance Evaluation

Replicate samples were collected at sites S355A and S4. All the analytes detected in the surface water had precision ≤ 30 percent relative percent difference. No pesticide analytes were detected in the equipment blanks performed at C25S99, S18C, S331, S65E, G123, S2, S7, S235, and G94D. All collected samples were shipped and all bottles were received.

Low concentrations of representative analytes from each pesticide group/method were added to laboratory water as well as to samples submitted. Table 7 lists parameters which did not meet the specified laboratory quality control requirements. The remainder of the analytes for each sample adhered to the targets for precision and accuracy as outlined in the FDEP Comprehensive Quality Assurance Plan. Organic quality assurance targets are set according to historically generated data or are adapted from the USEPA with slight modifications or internal goals, based on FDEP limited data. Parameters with low or high recoveries indicate that the sample matrix interferes with these analyses and interpretation of the respective analytical results should consider this effect.

Glossary

- LD₅₀: The dosage which is lethal to 50 percent of the terrestrial animals tested within a short (acute) exposure period, usually 24 to 96 hours.
- LC₅₀: A concentration which is lethal to 50 percent of the aquatic animals tested within a short (acute) exposure period, usually 24 to 96 hours.
- EC₅₀: A concentration necessary for 50 percent of the aquatic species tested to exhibit a toxic effect short of mortality (e.g., swimming on side or upside down, cessation of swimming) within a short (acute) exposure period, usually 24 to 96 hours.

K_{oc}: The soil/sediment partition or sorption coefficient normalized to the fraction of organic carbon in the soil. This value provides an indication of the chemical's tendency to partition between soil organic carbon and water.

Bioconcentration Factor:

The ratio of the concentration of a contaminant in an aquatic organism to the concentration in water, after a specified period of exposure via water only. The duration of exposure should be sufficient to achieve a near steady-state condition.

Soil or water half-life:

The time required for one-half the concentration of the compound to be lost from the water or soil under the conditions of the test.

Method Detection Limits (MDLs):

The minimum concentration of an analyte that can be detected with 99 percent confidence of its presence in the sample matrix.

Practical Quantitation Limits (PQLs):

The lowest level of quantitation that can be reliably achieved within specified limit of precision and accuracy during routine laboratory operating conditions. The PQLs are further verified by analyzing spike concentrations whose relative standard deviation in 20 fortified water samples is < 15 percent. In general, PQLs are 2 to 5 times larger than the MDLs.

Threshold Effects Concentration (TEC):

The threshold effects concentration is intended to identify concentrations below which harmful effects to freshwater sediment-dwelling organisms are unlikely to be observed.

Probable Effects Concentration (PEC):

The probable effects concentration is intended to identify concentrations above which harmful effects to sediment-dwelling organisms are likely to be frequently or always observed.

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Figure 1. South Florida Water Management District Pesticide Monitoring Network.

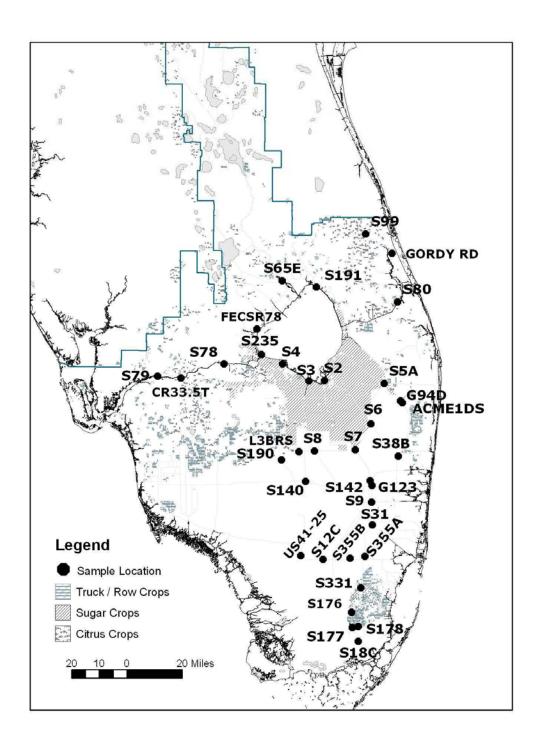


Table 1. Method detection limits (MDLs) and practical quantitation limits (PQLs) for May 2005 sampling event.

Pesticide or metabolite	Water: range of MDLs PQLs (µg/L)	Sediment: range of MDLs - PQLs (µg/Kg)	Pesticide or metabolite	Water: range of MDLs PQLs (µg/L)	Sediment: range of MDLs PQLs (µg/Kg)
2,4-D	0.2 - 0.6	8.3 - 210	endosulfan sulfate	0.0046 - 0.11	0.83 - 27
2,4,5-T	0.2 - 0.6	8.3 - 210	endrin	0.0095 - 0.04	2.1 - 68
2,4,5-TP (silvex)	0.2 - 0.6	8.3 - 210	endrin aldehyde	0.0042 - 0.018	0.83 - 27
acifluorfen	0.2 - 0.6	8.3 - 210	ethion	0.0095 - 0.04	2.1 - 68
alachlor	0.048 - 0.21	25 - 800	ethoprop	0.0095 - 0.04	2.1 - 68
aldrin	0.0019 - 0.0084	0.42 - 14	fenamiphos (nemacur)	0.038 - 0.16	8.3 - 270
ametryn	0.0095 - 0.072	2.1 - 68	fonofos (dyfonate)	0.019 - 0.084	4.2 - 140
atrazine	0.0095 - 0.19	2.1 - 68	heptachlor	0.0023 - 0.010	0.42 - 14
atrazine desethyl	0.0095 - 0.068	N/A	heptachlor epoxide	0.0019 - 0.0084	0.42 - 14
atrazine desisopropyl	0.0095 - 0.068	N/A	hexazinone	0.0095 - 0.19	2.1 - 68
azinphos methyl (guthion)	0.019 - 0.084	6.2 - 200	imidacloprid	0.2 - 0.6	N/A
α BHC (alpha)	0.0021 - 0.038	0.42 - 14	linuron	0.2 - 0.6	8.3 - 200
β BHC (beta)	0.0032 - 0.014	0.42 - 35	malathion	0.029 - 0.12	6.2 - 200
δ BHC (delta)	0.0019 - 0.0084	0.83 - 27	metalaxyl	0.048 - 0.21	N/A
γ BHC (gamma) (lindane)	0.0019 - 0.0084	0.42 - 14	methamidophos	N/A	21 - 680
bromacil	0.038 - 0.16	8.3 - 270	methoxychlor	0.0095 - 0.044	2.1 - 68
butylate	0.019 - 0.084	N/A	metolachlor	0.057 - 0.25	21 - 680
carbophenothion (trithion)	0.015 - 0.064	2.1 - 68	metribuzin	0.019 - 0.084	4.2 - 140
chlordane	0.019 - 0.084	6.2 - 200	mevinphos	0.057 - 0.25	8.3 - 270
chlorothalonil	0.015 - 0.064	2.1 - 68	mirex	0.011 - 0.048	1.7 - 56
chlorpyrifos ethyl	0.0095 - 0.04	2.1 - 68	monocrotophos (azodrin)	N/A	21 - 680
chlorpyrifos methyl	0.0095 - 0.04	4.2 - 140	naled	0.076 - 0.33	33 - 1,100
cypermethrin	0.019 - 0.084	2.1 - 68	norflurazon	0.019 - 0.084	4.2 - 140
DDD-P,P'	0.0046 - 0.020	0.83 - 27	parathion ethyl	0.019 - 0.084	6.2 - 200
DDE-P,P'	0.0038 - 0.023	0.83 - 27	parathion methyl	0.019 - 0.084	6.2 - 200
DDT-P,P'	0.0057 - 0.025	1.2 - 40	PCB	0.019 - 0.084	8.3 - 600
demeton	0.11 - 0.48	42 - 1,400	permethrin	0.015 - 0.064	2.5 - 80
diazinon	0.019 - 0.084	4.2 - 140	phorate	0.0095 - 0.04	2.1 - 68
dicofol (kelthane)	0.042 - 0.18	6.2 - 200	prometryn	0.019 - 0.084	6.2 - 200
dieldrin	0.0019 - 0.0084	0.42 - 21	prometon	0.019 - 0.084	N/A
disulfoton	0.019 - 0.084	4.2 - 140	simazine	0.0095 - 0.04	2.1 - 68
diuron	0.2 - 0.6	8.3 - 200	toxaphene	0.095 - 0.40	31 - 1,000
α endosulfan (alpha)	0.0038 - 0.016	0.42 - 24	trifluralin	0.0076 - 0.033	1.7 - 56
β endosulfan (beta)	0.0038 - 0.016	0.42 - 14		<u> </u>	

N/A - not analyzed

Table 2. Summary of pesticide residues (μ g/L) above the method detection limit found in surface water samples collected by SFWMD in May 2005.

Date	Site	Flow	2,4-D	ametryn	atrazine	atrazine desethyl	atrazine desisopropyl	bromacil	diuron	endosulfan sulfate	hexazinone	metolachlor	norflurazon	simazine	Number of compounds detected at site
5/23/2005	C25S99	N	-	-	0.015 I	-	_	0.72	-	-	0.011 l	-	1.1	0.11	5
0.20.200	S18C	N	-	-	0.084	-	-	-		-	-	-	-	-	1
	GORDYRD		-	-	-	-	-	0.15 I	-	-	-	-	0.50	0.12	3
	S178	N	-	-	-	-	-	-	-	0.035	-	-	-	-	1
	S177	Υ	-	-	0.11	0.012 I	-	-	-	-	_	-	-	-	2
	S80	Υ	-	-	0.15	0.020 I	-	-	-	-	_	-	0.037 I	-	3
	S176	Υ	-	-	0.086	-	-	-	-	-	_	-	-	-	1
	S331	N	-	-	0.048	-	-	-	-	-	0.011 I	-	-	-	2
	S191	N	3.3	-	0.031 I	-	-	-	-	-	-	-	-	-	2
	S65E	Υ	-	-	0.088	0.010 I	-	-	•	-	-	-	-	0.011 I	3
5/24/2005	FECSR78	-	-	-	0.082	-	-	-	-	-	0.024 l	-	-	-	2
	S355B	N	-	-	0.099	-	-	-	•	-	-	-	-	-	1
	S355A	N	-	-	0.014 l *	-	-	-	-	-	-	-	-	-	1
	S4	N	-	-	0.19 *	0.025 I *	-	-	-	-	0.029 I *	-	-	-	3
	S12C	N	-	-	0.012 I	-	-	-	ı	-	-	-	•	-	1
	US41-25	Υ	-	-	-	-	-	-	·	-	-	-	-	-	0
	S31	N	-	-	0.058	0.010 l	-	-	·	-	-	-	-	-	2
	S9	N	-	-	-	-	-	-	-	-	-	-	-	-	0
	S3	R	-	-	0.19	0.026 I	-	-	ı	-	0.030 I	-	1	-	3
	G123	N	-	0.016 I	0.099	0.013 I	-	-	·	-	-	-	-	-	3
	S2	R	-	-	0.19	0.025 I	-	-	-	-	0.034 I	-	-	-	3
5/25/2005	S142	Υ	-	0.015 I	0.080	0.022 I	-	-	-	-	0.011 I	-	-	-	4
	S140	N	-	-	0.030 I	0.011 l	-	-	-	-	-	-	0.083	-	3
	S190	N	-	-	0.034 I	-	-	-	-	-	-	-	0.025 I	-	2
	S79	Υ	-	-	0.20	0.024 l	-	-	-	-	0.027 l	-	0.026 I	0.010 I	5
	L3BRS	Υ	-	0.010 I	0.24	0.029 I	-	-	-	-	0.013 l	-	-	-	4
	S8	N	-	0.013 I	0.33	0.052	-	-	-	-	0.011 l	-	-	-	4
	CR33.5T	R	-	-	0.19	0.023 I	-	-	-	-	0.027 l	-	0.024 I	0.010 I	5
	S7	N	-	0.017 I	0.73	0.11	0.017 I	-	-	-	-	0.11 I	-	-	5
	S78	Υ	-	-	0.17	0.030 I	-	-	-	-	0.023 I	-	-	-	3
	S235	N	-	-	0.11	-	-	-	-	-	0.019 l	-	-	-	2
5/27/2005	S38B	N	-	-	3.3	0.20	0.027 I	-	-	-	-	-	-	0.010 I	4
	S6	Υ	-	-	1.5	0.041	-	-	-	-	0.013 I	0.082 I	-	-	4
	S5A	N	-	-	0.21	0.027 I	-	-	-	-	0.025 I	-	1	0.010 I	4
	ACME1DS	Υ	-	0.022	0.21	0.030 I	-	-	-	-	0.23	-	-	-	4
	G94D	Υ	-	-	0.062	-	-	-	0.78	-	1.7	-	-	-	3
	ber of compou etections	nd	1	6	32	20	2	2	1	1	17	2	7	7	98

N - no Y - yes R - reverse; - denotes that the result is below the MDL; * results are the average of replicate samples I - value reported is less than the practical quantitative limit, and greater than or equal to the method detection limit.

Table 3. Summary of pesticide residues (µg/Kg) above the method detection limit found in sediment samples collected by SFWMD in May 2005.

Date	Site	Flow	aldrin	ametryn	atrazine	bromacil	chlordane	DDD-P,P'	DDE-P,P'	DDT-P,P'	dieldrin	alpha endosulfan	beta endosulfan	endosulfan sulfate	PCB-1242	PCB-1254	Number of compounds detected at site
5/23/2005	S178	N	-	-	-	-	-	-	12 I	-	ı	5.9 l	8.7	63	-	-	4
	S177	Υ	-	-	-	-	-	-	3.9 I	-	-	1.7 I	2.6 I	4.9 l	-	-	4
	S80	Υ	-	-	-	-	-	-	3.1 I	-	-	-	-	-	70 I	-	2
5/24/2005	S4	N	-	10 I *	-	-	-	-	8.9 l *	-	-	-	-	-	-	-	2
	S3	R	-	-	-	-	50	12 I	44	-	-	-	-	-	-	-	3
	G123	Ν	-	-	-	82	-	-	3.8 I	-	-	-	-	-	-	-	2
	S2	R	2.9 I	16 I	•	-	80	33	170	13 I	ı	-	ı	ı	-	-	6
5/25/2005	S142	Υ	-	-	•	-	-	-	8.2 I	-	ı	-	ı	ı	-	-	1
	S79	Υ	-	-	•	-	-	-	8.4 I	-	2.4 l	-	ı	ı	89 I	-	3
	S8	N	-	-	•	-	-	-	2.9 I	-	ı	-	ı	ı	-	-	1
	S7	Ν	-	-	-	-	-	-	1.8 I	-	-	-	-	-	-	19 I	2
	S78	Υ	-	-	-	-	-	-	1.0 I	-	-	-	-	-	-	-	1
5/27/2005	S6	Υ	-	15 I *	-	-	57 *	28 *	82 *	-	-	-	1	-	101 *	-	5
	S5A	N	-	18 I	16 I	-	38	22	65	-	3.3 I	-	1	-	-	-	6
Total n	umber of d detection		1	4	1	1	4	4	14	1	2	2	2	2	3	1	42

N - no Y - yes R - reverse; - denotes that the result is below the MDL; * results are the average of replicate samples

Values in bold, italicized font are at a concentration that harmful effects to sediment-dwelling organisms are likely to be frequently or always observed.

I - value reported is less than the practical quantitative limit, and greater than or equal to the method detection limit.

Table 4. Selected properties of pesticides found in May 2005 sampling event.

	Surface	Ground	LD ₅₀		Water				Soil			
	Water	Water	acute rats		Solubility		Soil	Co	nservati	on		
	Standards	Guidance	oral	EPA	(WS)	Koc	Half-life		Service		Volatility	
	FAC 62-302	Conc.	(mg/kg)	Carcinogenic	(mg/L)	(mL/g)	(days)	(SC	S) rating	(2)	frrom	Bioconcentration
Common Name	(µg/L)	(µg/L)	(1)	Potential	(2, 3)	(2, 3)	(2, 3)	LE	SA	SS	Water	Factor (BCF)
2,4-D (acid)	(100)	70**	375	D	890	20	10	М	S	M		13
aldrin	3	0.05	38-67	B2	0.05	48,500	-	-	-	-	S	3,348
ametryn	-	63	1,110	D	185	300	60	М	М	М		33
atrazine	-	3**	3,080	С	33	100	60	L	M	L		86
bromacil	-	90	5,200	С	700	32	60	L	M	M		15
chlordane	0.0043	2**	365-590	B2	0.056	3,800	-	-	-	-		3,141
DDD, p,p'	-	0.1	3,400	-	0.055	239,900	-	-	-	-	ı	3,173
DDE, p,p'	-	0.1	880	-	0.065	243,220	-	-	-	-	S	2,887
DDT, p,p'	0.001	0.1	113	-	0.00335	140,000	-	-	-	-	ı	15,377
diuron	-	14	3,400	D	42	480	90	М	M	L	ı	75
dieldrin	0.0019	0.1	37 - 87	B2	0.14	10,000 est.	-	-	-	-		1,873
endosulfan alpha	0.056	0.35	70	-	0.53	12,400	50	XS	L	M	S	884
endosulfan beta	-	0.35	70	-	0.28	ı	-	-	-	-	S	1,267
endosulfan sulfate	-	0.3	-	-	0.117	ı	-	-	-	-		2,073
hexazinone	-	231	1,690	D	33,000	54	90	L	M	М		2
metolachlor	-	1,050	2,780	С	530	200	90	L	M	М		18
norflurazon	-	280	9,400	С	28	700	90	М	M	L		94
PCB's	0.014	0.5**	-	B2	-	-	-	-	-	-	-	-
simazine	-	4**	>5,000	С	6.2	130	60	L	M	М	ı	221

SCS Ratings are pesticide loss due to leaching (LE), surface adsorption (SA) or surface solution (SS) and grouped as large(L), medium (M), small (S) or extra small (XS) Volatility from water: R = rapid, I = insignificant, S = significant

Bioconcentration Factor (BCF) calculated as BCF = $10^{(2.791 - 0.564 \log WS)}$ (4)

B2: probable human carcinogen; C: possible human carcinogen; D: not classified; E: evidence of non-carcinogen for humans (5)

FDEP surface water standards (4/95) for Class III waters except Class I in ()

Note: endosulfan usually considered the sum of alpha and beta isomers

- (1) Hartley, D. and H. Kidd. (Eds.) (1987).
- (2) Goss, D. and R. Wauchope. (Eds.) (1992).
- (3) Montgomery, J.H. (1993).
- (4) Lyman, W.J., W.F. Reehl, and D.H. Rosenblatt. (1990).
- (5) U.S. Environmental Protection Agency (1996).

^{**} primary standard

Table 5. Toxicity of pesticides found in the May 2005 sampling event to freshwater aquatic invertebrates and fishes (µg/L).

	48-hr E	C ₅₀			96-hr LC	C ₅₀			96-hr LC	50			96-hr LC	50			96-hr LC	60			96-hr LC	50		
	\^/-t #	_	acute	chronic	Fathea	d			Diversit				Largemou	uth			Rainbow Tr	out			Channe	el		i
	Water fl	ea	toxicity	toxicity	Minnow	(#)			Bluegil	l			Bass				(#)				Catfish	ı		
common	Daphn	ia	(*)	(*)	Pimepha	les	acute	chronic	Lepomi	S	acute	chronic	Micropter	us	acute	chronic	Oncorhynch	nus	acute	chronic	Ictaluru	s	acute	chronic
name	magn	а			promela	as	toxicity	toxicity	macrochii	ันร	toxicity	toxicity	salmoide	es	toxicity	toxicity	mykiss		toxicity	toxicity	punctatu	ıs	toxicity	toxicity
2,4-D	25,000	(7)	8,333	1,250	133,000	(7)	44,333	6,650	180,000	(8)	60,000	9,000	-		-	-	100,000	(4)	33,333	5,000	-		-	-
	-		-	-	-		-	-	900 (48 hr.)	(6)			-		-	-	110,000	(7)	36,667	5,500	-		-	-
aldrin	-		-	-	28	(5)	9.3	1.4	13	(5)	4.3	0.65	-		-	-	17.7	(5)	5.9	0.89	-		-	-
ametryn	28,000	(7)	9,333	1,400	-		-	ı	4,100	(4)	1,367	205	-		-	-	8,800	(4)	2,933	440	-		-	-
atrazine	6900	(7)	2,300	345	15,000	(7)	5000	750	16,000	(4)	5,333	800	•		-	-	8,800	(4)	2,933	440	7,600	(4)	2,533	380
bromacil	-		-	-	-		-	ı	127,000	(5)	42,333	6,350	-		-	-	36,000	(5)	12,000	1,800	-		-	-
chlordane	-		-	-	-		-	ı	70	(5)	23	3.5			-	-	90	(5)	30	5			-	-
DDD, p,p'	3,200	(6)	1,067	160	4,400	(1)	1467	220	42	(1)	14	2.1	42	(1)	14	2.1	70	(1)	23.3	3.5	1,500	(1)	500	75
DDE, p,p'	-		-	ı	-		-	ı	240	(1)	80	12			-	-	32	(1)	10.7	1.6	-		-	-
DDT, p,p'	-		-	ı	19	(5)	6.3	0.95	8	(5)	2.7	0.4	2	(5)	0.7	0.10	7	(5)	2.3	0.35	16	(5)	5.3	0.8
diuron	1,400	(7)	467	70	14,200	(7)	4,733	710	5,900	(4)	1,967	295	-		-	-	5,600	(4)	1,867	280	-		-	-
dieldrin	-		-	ı	16	(5)	5.3	0.80	8	(4)	2.7	0.4	•		-	-	10	(5)	3.3	0.5	4.5	(5)	1.5	0.23
endosulfan	166	(7)	55	8	1	(1)	0.3	0.05	1	(1)	0.33	0.05	•		-	-	1	(1)	0.33	0.050	1	(1)	0.3	0.05
	-		-	ı	-		-	ı	2	(3)	0.67	0.10	•		-	-	3	(2)	1	0.15	1.5	(7)	0.5	0.08
	-		-	-	-		-	-	-		-	-	-		-	-	1	(3)	0.33	0.050	-		-	-
	-		-	-	-		-	-	-		-	-	-		-	-	0.3	(5)	0.10	0.015	-		-	-
hexazinone	151,600	(7)	50,533	7,580	274,000	(4)	91,333	13,700	100,000	(7)	33,333	5,000	-		-	-	180,000	(7)	60,000	9,000	-		-	-
metolachlor	23,500	(7)	7,833	1,175	-		-	-	15,000	(4)	5,000	750	-		-	-	2,000	(4)	667	100	4,900	(5)	1,633	245
norflurazon	15,000	(7)	5,000	750	-		-	-	16,300	(7)	5,433	815	-		-	-	8,100	(7)	2,700	405	>200,000	(4)	>67,000	>10,000
simazine	1,100	(7)	367	55	100,000	(7)	33,333	5,000	90,000	(4)	30,000	4,500	-		-	-	100,000	(7)	33,333	5,000	-		-	-

^(*) Florida Administrative Code (FAC) 62-302.200, for compounds not specifically listed, acute and chronic toxicity standards are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, where the 96 hour LC50 is the lowest value which has been determined for a species significant to the indigenous aquatic community.

- (1) Johnson, W. W. and M.T. Finley (1980).
- (2) U.S. Environmental Protection Agency (1977).
- (3) Schneider, B.A. (Ed.) (1979).
- (4) Hartley, D. and H. Kidd. (Eds.) (1987).
- (5) Montgomery, J.H. (1993).
- (6) Verschueren, K. (1983).
- (7) U.S. Environmental Protection Agency (1991).
- (8) Mayer, F.L., and M.R. Ellersieck (1986).

^(#) Species is not indigenous. Information is given for comparison purposes only.

Table 6. Atrazine desethyl/atrazine ratio (DAR) data for May 2005 sampling event.

			atrazine		atrazine desethyl		
Date	Site	Flow*	ug/L	moles/L	ug/L	moles/L	DAR
5/23/2005	S177	Υ	0.11	5.10E-10	0.012	6.40E-11	0.1
	S80	Υ	0.15	6.95E-10	0.020	1.07E-10	0.2
	S65E	Υ	0.088	4.08E-10	0.010	5.33E-11	0.1
5/24/2005	S4	N	0.19	8.81E-10	0.025	1.33E-10	0.2
	S31	N	0.058	2.69E-10	0.010	5.33E-11	0.2
	S3	R	0.19	8.81E-10	0.026	1.39E-10	0.2
	G123	N	0.099	4.59E-10	0.013	6.93E-11	0.2
	S2	R	0.19	8.81E-10	0.025	1.33E-10	0.2
5/25/2005	S142	Υ	0.080	3.71E-10	0.022	1.17E-10	0.3
	S140	N	0.030	1.39E-10	0.011	5.86E-11	0.4
	S79	Υ	0.20	9.27E-10	0.024	1.28E-10	0.1
	L3BRS	Υ	0.24	1.11E-09	0.029	1.55E-10	0.1
	S8	N	0.33	1.53E-09	0.052	2.77E-10	0.2
	CR33.5T	R	0.19	8.81E-10	0.023	1.23E-10	0.1
	S7	N	0.73	3.38E-09	0.11	5.86E-10	0.2
	S78	Υ	0.17	7.88E-10	0.030	1.60E-10	0.2
5/27/2005	S38B	N	3.3	1.53E-08	0.20	1.07E-09	0.1
	S6	Υ	1.5	6.95E-09	0.041	2.19E-10	0.0
	S5A	N	0.21	9.74E-10	0.027	1.44E-10	0.1
	ACME1DS	Υ	0.21	9.74E-10	0.030	1.60E-10	0.2
				DAR	All sites	Flow only sites	No flow sites
	* N - no; Y - ye	es; R - r	everse	average	0.2	0.2	0.2
				median	0.2	0.1	0.2
				minimum	0.0	0.0	0.1
				maximum	0.4	0.3	0.4

Table 7. Laboratory Quality Control Failures for May 2005 Sampling Event.

	Compound											
Site	acifluorfen	monocrotphos	metalaxyl	malathion								
S176	MS - SD	LCS -SD	-	MS - SD								
S177	MS - SD	LCS -SD	-	MS - SD								
S178	MS - SD	LCS -SD	-	MS - SD								
S18C	MS - SD	LCS -SD	-	MS - SD								
S331	MS - SD	LCS -SD	-	MS - SD								
FECSR78	MS - SD	LCS -SD	-	MS - SD								
S12C	MS - SD	LCS -SD	-	MS - SD								
S191	MS - SD	LCS -SD	-	MS - SD								
S235	MS - SD	LCS -SD	=	=								
S31	MS - SD	LCS -SD	-	MS - SD								
S65E	MS - SD	LCS -SD	-	MS - SD								
S355A	MS - SD	LCS -SD	_	MS - SD								
S355B	MS - SD	LCS -SD	-	MS - SD								
S78	MS - SD	LCS -SD	-	-								
S79	MS - SD	LCS -SD	=	-								
S80	MS - SD	LCS -SD	_	MS - SD								
S9	MS - SD	LCS -SD	-	-								
US41-25	MS - SD	LCS -SD	_	MS - SD								
C25S99	MS - SD	LCS -SD	-	MS - SD								
G123	MS - SD	LCS -SD	-	-								
L3BRS	MS - SD	LCS -SD	-	-								
S140	MS - SD	LCS -SD	-	-								
S142	MS - SD	LCS -SD	-	-								
S190	MS - SD	LCS -SD	-	-								
S2	MS - SD	LCS - SD	-	MS - SD								
S3	MS - SD	LCS - SD	-	MS – SD								
S4	MS - SD	LCS - SD	-	MS – SD								
S7	MS - SD	LCS -SD	-	-								
S8	MS - SD	LCS -SD	-	-								
ACME1DS	MS - SD	LCS -SD	LCS – W	-								
G94D	MS - SD	LCS -SD	LCS – W	-								
S38B	MS - SD	LCS -SD	LCS – W	-								
S5A	MS - SD	LCS -SD	LCS – W	-								
S6	MS - SD	LCS -SD	LCS – W	-								

MS: matrix spike; RPD: relative percent difference; LCS: laboratory control sample; W: water; SD: sediment